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(54) WET TRANSFER PRINTING PROCESS FOR THE COLOURATION OF CELLULOSE TEXTILE MATERIALS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the colouration of cellulose textile materials by the process of wet transfer printing using a particular class of reactive dyestuff which is valuable for this purpose.

In the process of wet transfer printing an appropriate dyestuff for the textile material concerned is incorporated into an ink which is then applied to a paper substrate using a conventional method of paper printing, after which the printed paper is dried. The resulting printed paper, which is commonly referred to as a transfer paper, is then placed in contact with the textile material, the printed surface of the paper being in contact with the textile material, and the two are then heated, whilst in contact, in the presence of water vapour or steam. When transfer of the dyestuff is complete the paper and textile material are separated, and the textile material is then subjected to a washing sequence.

Dyestuffs containing fibre-reactive systems, i.e. the well known class of Reactive Dyestuffs can be applied to cellulose textile by the above process provided that an alkaline treatment is included in order that fixation of the reactive dyestuff is obtained. This can be conveniently effected by treating the cellulose textile material with an aqueous solution of an alkali prior to transfer being effected. Such a process is described and claimed in British Specification No. 1227271. However, the use of reactive dyestuffs in the process of wet transfer printing results in a number of problems. Whilst the dyestuffs must be sufficiently reactive so that adequate fixation (and hence good colour value) is achieved on the cellulose textile material in a reasonable processing time which is usually of the order of 10 to 60 seconds, the dyestuffs must be sufficiently stable so that they are not hydrolysed, or at least not hydrolysed to any significant extent during their application to the paper or whilst the resulting transfer paper is stored, and during the actual transfer of the dyestuff from the transfer paper to the cellulose textile material under the hot, humid conditions. Specification No. 122721 disclosed that reactive dyestuffs containing chloro- or bromo-pyrimidinylamino groups can be used in the process, but such dyestuffs, whilst having adequate stability, are only of low reactivity on cellulose textile materials so that adequate fixation in a reasonable time cannot be achieved unless the cellulose textile material, after transfer has taken place, is subjected to a separate steaming treatment.

It has been found that this disadvantage can be overcome by the use of reactive dyestuffs which contain a difluorochloropyrimidinylamino group.

According to the present invention there is provided an improved process for the colouration of cellulose textile materials which comprises:-

(a) printing paper with an ink containing a reactive dyestuff having a difluorochloropyrimidinylamino group, and thereafter drying the paper,

(b) impregnating a cellulose textile material with an aqueous solution of alkali,

(c) contacting the printed paper with the impregnated cellulose textile material, the printed surface of the paper being in contact with the cellulose textile material, and heating the two whilst in contact at a temperature above 80°C,

(d) separating the printed paper and the cellulose textile material, subjecting the cellulose textile material to a washing sequence, and finally drying.

The actual process of transferring the dyestuff from the printed paper to the cellulose

textile material can be carried out by batchwise and continuous modes of operation. Thus for batchwise operation a piece of the transfer paper (i.e. the printed paper obtained by stage (a)) is placed in contact with a piece of cellulose textile material which has previously been impregnated with an aqueous solution of an alkali, and the two then placed together in a press, which has been heated to the appropriate temperature, for the requisite time. The so-called cellulose textile material is then separated from the used transfer paper and subjected to a washing sequence.

In a continuous mode of operation the transfer paper and the cellulose textile material which has been impregnated with the aqueous solution of the alkali are brought into contact together before being passed round a rotating heated calender, after which the two are separated and the cellulose textile material subjected to the washing sequence. When using such a calender the speed of rotation and the diameter of the calender are such that adequate transfer and fixation of the dyestuff is obtained during the time that any particular portion of the cellulose textile material is in contact with the calender. A particularly valuable machine on which the transfer and subsequent washing sequence can be carried out in a continuous manner is the "Dewprint" Machine which is available from Dinting Engineering Ltd (Dewprint is a trade mark).

In cases where the reactive dyestuff is very highly reactive there is a possibility that too much alkali in the textile material may cause premature hydrolysis of a portion of the dyestuff before it can react with the cellulose. In such cases the concentration of alkali in the aqueous impregnation solution may be significantly reduced or the alkali impregnation step (b) of the process may be omitted, an alkali treatment, or a further alkali treatment, then being applied by any suitable known method at a suitable stage after the fabric has been contacted with the printed paper in step (c).

The reactive dyestuffs used in the process of the invention can be dyestuffs of any of the conventional classes, such as azo, including monoazo, disazo and metallised azo dyestuffs, anthraquinone, nitro, phthalocyanine, formazan and triphendioxazine dyestuffs which contain a difluorochloropyrimidinylamino group. Such dyestuffs are in general known compounds and are obtained, for example, by reacting the corresponding dyestuff containing a primary or secondary amino group with 2: 4: 6-trifluoro-5-chloropyrimidine.

The inks used to obtain the transfer papers consist essentially of a reactive dyestuff or dyestuffs, as previously defined, a binder, and a liquid medium in which the binder is soluble. When the liquid is water then the binder is a water-soluble binder such as sodium alginate. Alternatively the liquid medium can be an organic liquid such as an aliphatic alcohol, a hydrocarbon, a ketone or an ester (or a mixture of one or more of such liquids), in which case a binder is used which is soluble in the said liquid. Preferred binders for such inks are alkyl celluloses such as ethyl cellulose and hydroxypropyl cellulose.

The resulting inks can be applied to a paper substrate on any of the conventional equipment used for printing paper using aqueous or solvent based inks.

The aqueous solution of the alkali preferably contains from 0.5 to 1.0% by weight of an alkali such as sodium bicarbonate, sodium carbonate, sodium hydroxide or potassium carbonate. If desired the said aqueous solution can contain other additives which assist the transfer and/or fixation of reactive dyestuffs, such as urea, sodium *m*-nitrobenzene sulphonate and tertiary amines such as 2: 2: 2-bicyclodiazaoctane.

The washing sequence to which the printed cellulose textile material is finally subjected can consist of any desired number of steps, for example a rinse in cold water, followed by "soaping" in a hot aqueous solution of soap or a synthetic detergent, and a final rinse in cold water.

If desired instead of using a 100% cellulose textile material there can be used a union consisting of a mixture of cellulose and synthetic fibres, preferably aromatic polyester fibres. In this event, in order that the synthetic fibres are simultaneously coloured, a disperse dyestuff or dyestuffs are also included in the ink used to print the paper in stage (c) of the process. The colouration of such unions forms a further feature of the present invention.

The aromatic polyester/cellulose union may also be coloured using the reactive dyestuff only, so that the polyester part of the union remains undyed.

The disperse dyestuffs can be any of the disperse dyestuffs which are commercially available or which are described in, for example, the Third Edition of the Colour Index (1971). Such disperse dyestuffs can be used in their commercially available forms which contain large amounts of water-soluble dispersing agents, or if preferred, particularly in the case of solvent based inks, they are used in concentrated form (i.e. they are free from such dispersing agents). A particularly valuable class of disperse dyestuffs for use in the process are those which contain at least two carboxylic acid ester groups, as any unfixed dyestuff on the textile material can be readily removed by treatment in a warm aqueous solution of an alkali without detriment to the reactive dyestuff used for colouring the cellulose fibres. When using this preferred class of disperse dyestuffs in the process it is preferred that the washing

sequence includes a rinse in an aqueous solution of an alkali having a pH above 8 and a temperature in the region of 50° to 85°C.

Examples of this preferred class of disperse dyestuffs are given in, for example, British Application No. 14783/74 (Serial No. 1456586).

When using mixtures of disperse and reactive dyestuffs in the process it is preferred that the two types of dyestuffs are so selected and are used in such relative amounts that the two types of fibre present in the unions are coloured to the same hue and to the same depth of shade.

By the process of the invention cellulose textile materials and unions of cellulose fibres and synthetic fibres, preferably aromatic polyester fibres, are coloured in a wide variety of shades, in which there is excellent reserve of any unprinted portions thereof, and the resulting colourations have excellent fastness properties.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

Example 1

An ink is prepared by dissolving 5 parts of the tetrasodium salt of the copper complex of 2-[2'-hydroxy-4'- [2"-methoxy- 3"-sulpho-5"- (difluorochloropyrimidinylamino) phenylazo] phenylazo]-1-naphthol-3: 6: 8-trisulphonic acid in 25 parts of water and then adding 70 parts of a 5% aqueous solution of sodium alginate. The resulting ink is then screen printed on to the glazed side of a 70 gm/sq.metre bleached Kraft paper, and the paper is then dried. (Kraft is a trade mark).

A mercerised woven cotton cloth is impregnated to 60% retention in an aqueous solution containing 1.0% of sodium carbonate and 5.0% of urea, and the impregnated cloth and printed paper are then continuously fed in contact round the heated cylinder of a "Dewprint" wet transfer printing machine, the time of passage being 60 seconds and the temperature of the cylinder being 115-120°C. After passage round the cylinder the cotton cloth is separated from the paper, is rinsed in cold water, treated for 10 minutes in an 0.3% aqueous solution of a synthetic detergent at 100°C, rinsed again in water, and is finally dried.

A navy blue print is thereby obtained.

Example 2

An ink is prepared by mixing together 50 parts of a 10% aqueous dispersion of 2-acetylamino-4- [N:N-di-(β-ethoxycarbonylethyl) amino] -4'-nitroazobenzene, 50 parts of urea, 350 parts of a 5% aqueous solution of sodium alginate and 525 parts of water, and then adding 25 parts of the trisodium salt of 2-[1'-sulpho-5'- (difluorochloropyrimidinyl-aminomethyl) naphthh-2'-ylazo-1-naphthol-3:6-disulphonic acid.

The ink is then printed on to the glazed side of a 55gm/sq.metre bleached Kraft paper, and the paper is dried. (Kraft is a trade mark).

A 67:33 aromatic polyester/cellulose woven cloth is impregnated to 50% retention in an aqueous solution containing 1.0% of sodium bicarbonate and 5.0% of urea, and the impregnated cloth and printed paper are then continuously fed whilst in contact round the heated cylinder of a "Dewprint" (Dewprint is a trade mark) wet transfer printing machine, the time of passage being 40 seconds, and the temperature of the cylinder being 115-120°C. After passage round the cylinder the cloth is separated from the paper, is rinsed in cold water, treated for 5 minutes in an 0.2% aqueous solution of sodium hydroxide at 85°C, rinsed again in water, and is finally dried.

A red print is thereby obtained.

Example 3

An ink is prepared by milling together 10 parts of the disodium salt of 1-(6':8'-disulphonaphth-2'-ylazo) -2-acetylamino-4- (difluorochloro- pyrimidinylamino) benzene, 0.1 parts of an alkyl-aryl sulphonate having an HLB value of 11.7±1 available from Honeywill Atlas Ltd, under the trade name G-3300. 4 parts of ethyl cellulose N7 and 185.9 parts of toluene, and the viscosity is then adjusted to 20-25 seconds (No.4 Ford cup) by addition of a toluene solution of ethyl cellulose. The ink is printed on to paper on a gravure printed machine. The resulting printed paper is then used to colour a mercerised woven cotton cloth as described in Example 1.

A yellow print is thereby obtained.

WHAT WE CLAIM IS:

1. A process for the colouration of cellulose textile materials which comprises:-

(a) printing paper with an ink containing a reactive dyestuff having a difluorochloropyrimidinylamino group, and thereafter drying the paper,

(b) impregnating a cellulose textile material with an aqueous solution of alkali,

(c) contacting the printed paper with the impregnated cellulose textile material, the printed surface of the paper being in contact with the cellulose textile material, and heating the two whilst in contact at a temperature above 80°C,

(d) separating the printed paper and the cellulose textile material, subjecting the cellulose textile material to a washing sequence, and finally drying.

2. A batchwise process as claimed in claim 1 wherein pieces of printed transfer paper and alkali-impregnated cellulose textile material are contacted in a press.

3. A continuous process as claimed in claim 1 wherein printed transfer paper and alkali-impregnated cellulose textile material are brought into contact together before being passed round a rotating heated calendar.

4. A process as claimed in any one of claims 1 to 3 wherein the transfer printing ink comprises a reactive dyestuff or dyestuffs as defined in claim 1, a binder and a liquid medium in which the binder is soluble.

5. A process as claimed in claim 4 wherein the liquid medium is water and the binder is sodium alginate.

6. A process as claimed in claim 4 wherein the liquid medium is an organic liquid.

7. A process as claimed in claim 6 wherein the organic liquid is an aliphatic alcohol, a hydrocarbon, a ketone or an ester, or a mixture of two or more of such liquids.

8. A process as claimed in claim 6 or claim 7 wherein the binder is an alkyl cellulose.

9. A process as claimed in claim 8 wherein the alkyl cellulose is ethyl cellulose or hydroxypropyl cellulose.

10. A process as claimed in any one of claims 1 to 9 wherein the aqueous alkali contains from 0.5 to 1.0% by weight of the alkali.

11. A process as claimed in claim 10 wherein the alkali is sodium bicarbonate, sodium carbonate, sodium hydroxide or potassium carbonate.

12. A process as claimed in any one of claims 1 to 11 wherein, in place of 100% cellulose textile material there is used a union consisting of a mixture of cellulose and aromatic polyester fibres, and the printing ink includes a disperse dyestuff or dyestuffs to simultaneously colour the aromatic polyester fibres.

13. A process as claimed in claim 12 wherein the disperse dyestuff containd at least two carboxylic acid ester groups.

14. A process as claimed in claim 13 wherein the washing sequence includes a rinse in an aqueous solution of an alkali having a pH above 8 and a temperature in the region of 50° to 85°C.

15. A process as claimed in any one of claims 12 to 14 wherein the reactive and disperse dyestuffs are selected and used in such relative amounts that the two types of fibres present in the unions are coloured to the same hue and to the same depth of shade.

16. A process for the colouration of cellulose textile materials substantially as hereinbefore described in the foregoing Examples.

17. Cellulose textile materials whenever coloured by a process as claimed in any one of the preceding claims.

Agents for the Applicants
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